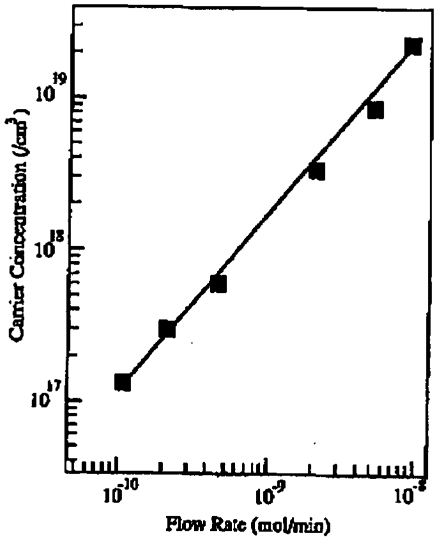

FIG. 7. Carrier concentrations of silicon-doped gallium nitride films as a function of the flow rate of silane (SiH_4). Reprinted from Nakamura *et al.* (1992c) with the permission of the Japanese Journal of Applied Physics.

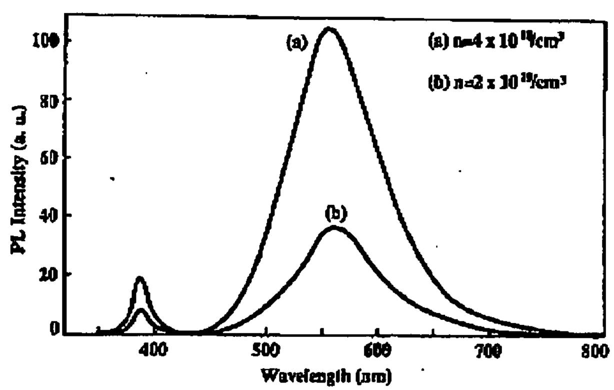

FIG. 8. Photoluminescence (PL) spectra of silicon-doped gallium nitride (GaN) films grown with GaN buffer layers under the same growth conditions except for the flow rate of silane (SiH_4). The flow rates for SiH_4 were (a) 2 nmol/min and (b) 10 nmol/min. The carrier concentrations were (a) 4×10^{18}/cm^3 and (b) 2×10^{19}/cm^3. Reprinted from Nakamura *et al.* (1992c) with the permission of the Japanese Journal of Applied Physics.

the realization of light-emitting devices, such as blue LEDs ar 1989, p-type GaN films were obtained using Mg doping and energy electron beam irradiation (LEEBI) treatment by means o for the first time (Amano *et al.*, 1989). After the growth, LEEBI was performed for Mg-doped GaN films to obtain a low-resisti GaN film. The hole concentration and lowest resistivity were 10 12 Ω·cm, respectively. These values were still insufficient for blue LDs and high-power blue LEDs. The effect of the LEEBI was considered to be Mg displacement by the energy of elec irradiation. At the first stage of as-grown Mg-doped GaN, the M in sites different from Ga sites where they act as acceptors. LEEBI treatment, the Mg atoms move to the exact Ga site.

In 1992, low-resistivity Mg-doped p-type GaN films were o N_2-ambient thermal annealing at temperatures above 400°C (N: *al.*, 1992d). Before thermal annealing, the resistivity of Mg-doped was approximately 1×10^6 Ω·cm. After thermal annealing at te above 700°C, the resistivity, hole carrier concentration, and h became 2 Ω·cm, 3×10^{17}/cm^3, and 10 cm^2/V·sec, respectively, a Fig. 9. In PL measurements, the intensity of the 750-nm D sharply decreased on thermal annealing at temperatures above 70 the change in resistivity, and the 450-nm blue emission showed a intensity at approximately 700°C for thermal annealing, as showr

Soon, a hydrogenation process whereby acceptor-H neutral are formed in p-type GaN films was proposed as a compensatic ism (Nakamura *et al.*, 1992a). Low-resistivity p-type GaN films, obtained by N_2-ambient thermal annealing or LEEBI treatmen resistivity as high as 1×10^6 Ω·cm after NH_3 ambient thermal a

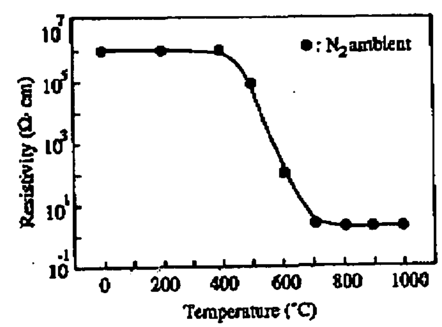

FIG. 9. Resistivity of as-grown magnesium-doped gallium nitride films as annealing temperature. N_2, nitrogen. Reprinted from Nakamura *et al.* (19 permission of the Japanese Journal of Applied Physics.

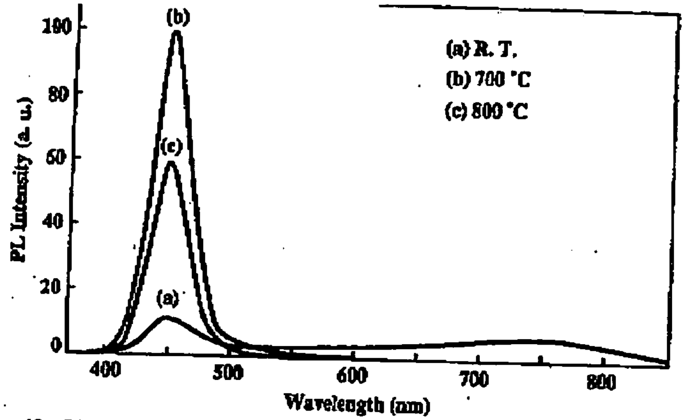

FIG. 10. Photoluminescence (PL) of as-grown magnesium-doped gallium nitride films that were annealed at different temperatures: (a) room temperature, (b) 700°C, and (c) 800°C. R.T., room temperature. Reprinted from Nakamura *et al.* (1992d) with the permission of the Japanese Journal of Applied Physics.

temperatures above 600°C. In the case of N_2 ambient thermal annealing at temperatures between room temperature and 1000°C, the low-resistivity p-type GaN films showed no change in resistivity, which was almost constant between 2 and 8 Ω·cm, as shown in Fig. 11.

Figure 12(a) shows the PL spectrum of 800°C N_2 ambient thermal-annealed GaN film, Fig. 12(b) shows the film after NH_3 ambient thermal annealing at 800°C for the sample in Fig. 12(a), and Fig. 12(c) shows the

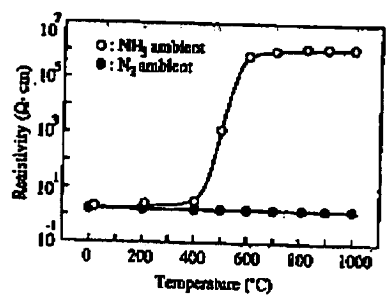

FIG. 11. The resistivity change in N_2 ambient thermal-annealed low-resistivity magnesium-doped gallium nitride films as a function of annealing temperature. The ambient gases, ammonia (NH_3) and nitrogen (N_2), were used for thermal annealing. Reprinted from Nakamura *et al.* (1992a) with the permission of the Japanese Journal of Applied Physics.

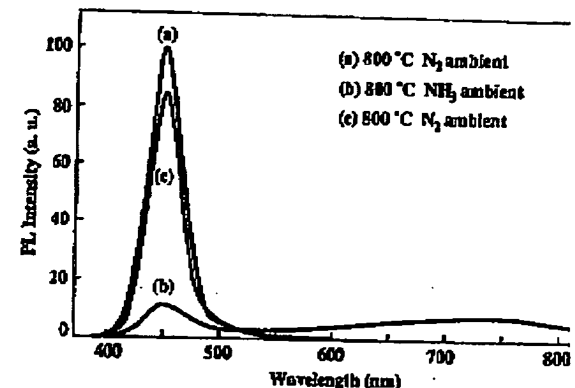

FIG. 12. Photoluminescence (PL) spectra of magnesium-doped gallium nitr that were continuously annealed under different conditions: (a) GaN film after ambient thermal annealing of the Mg-doped GaN film; (b) GaN film after 8 ambient thermal annealing of the GaN film in (a); (c) GaN film after 800 thermal annealing of the GaN film in (b). Reprinted from Nakamura *et al.* (1 permission of the Japanese Journal of Applied Physics.

film after N_2 ambient thermal annealing at 800°C for the san 12(b). Before NH_3 ambient thermal annealing, the intensity emission is strong, and the broad *DL* emission is not observec 750 nm (Fig. 12(a)). After NH_3 ambient thermal annealing at 8C sample in Fig. 12(a), the intensity of the blue emission becomes the *DL* emission around 750 nm appears (Fig. 12(b)). The Pl recovers after N_2 ambient thermal annealing at 800°C. These cha PL spectra were found to be reversible with a change in the ambient gas from NH_3 to N_2, as is the case with the resistivity

These results indicate that atomic hydrogen produced by NH tion at temperatures above 400°C is related to the acceptor cor mechanism. A hydrogenation process whereby acceptor-H ne plexes are formed in p-type GaN films was proposed. The foi acceptor-H neutral complexes causes acceptor compensation, an weak blue emission in PL. At temperatures above 400°C, the diss NH_3 into hydrogen atoms occurs at the surface of GaN filr dangling bonds exist mainly at the surface, and the atomic hydrc diffuses into the GaN films because the number of hydrogen atc great at the surface and the size of hydrogen atoms is very small. atomic hydrogen, produced by dissociation of NH_3 at temperatu 400°C, diffuses into p-type GaN films. Second, the formation of a neutral complexes, that is, Mg–H complexes in GaN films occ